Bioelectrochemistry 77 (2009) 37–42

Contents lists available at ScienceDirect

Bioelectrochemistry

journal homepage: www.elsevier.com/locate/bioelechem

Effect of size and protein environment on electrochemical properties of gold nanoparticles on carbon electrodes

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ARTICLE INFO

Article history:
Received 10 February 2009
Received in revised form 1 June 2009
Accepted 3 June 2009
Available online 11 June 2009

Keywords:
Gold nanoparticles
Proteins
Square-wave voltammetry
Carbon nanotubes
Atomic force microscopy

ABSTRACT

We studied the electrochemical properties of gold nanoparticles (GNPs) and their complexes with proteins using square-wave voltammetry. Effect of the nanoparticle size and detection procedure was explored upon the oxidation of GNPs on a glassy carbon electrode (GCE). For pre-characterized GNPs of 13, 35 and 78 nm diameter, the oxidation peak potential was +0.98, +1.03 and +1.06 V vs. Ag/AgCl, respectively. The conjugation of GNPs with four different proteins was verified by UV–Vis spectroscopy and atomic force microscopy indicated the formation of protein shells around GNPs. This process hampered the oxidation of GNPs on bare GCE causing pronounced decrease in the current response by an average factor of 72. GCE modification with carbon nanotubes weakly influenced the sensitivity of GNP detection but resulted in a 14.5-fold signal increase averaged for all GNP–protein complexes. The acidic dissolution and electrodeposition of GNPs or their complexes adsorbed on GCE allowed superior signal amplification directly proportional to nanoparticle size. The results are useful for the optimization of voltammetric analysis of GNP–protein complexes and can be extended to the characterization of other metal nanostructures and their complexes with biological components.

1. Introduction

Gold nanoparticles (GNPs) are key nanomaterials intensively studied in different fields of biology and medicine. Particularly, the electronic and optical properties of GNPs are widely exploited for imaging biological objects using microscopy techniques [1,2]. There is a growing interest in biomedical applications of non-spherical gold nanostructures, such as nanorods and nanoshells, which exhibit altered extinction and scattering parameters [2] and cellular uptake mechanism [3] compared to spherical GNPs. Such nanostructures are promising both for the visualization of living cells in vitro and in vivo and their directed damage by means of hyperthermia [4].

The development of biological sensors is another important application of GNPs. In particular, GNPs are used as optical [5–8] and electrochemical [9–12] probes for detecting biomolecules and amplifying biosensor signal. Generally, GNPs improve the analytical performance of biosensor methods by increasing their sensitivity, selectivity and flexibility. To date, different GNP-based biosensors for the analysis of immune components [5,7,8,11,12] and nucleic acids [6,9,10] have been proposed. There are optical biosensors for real-time detection of biomolecule interactions accompanied with a change of localized plasmon resonance spectra of GNPs in the solution or on the transducer surface [7,8]. The susceptibility of GNPs to non-specific adsorption of biological components decreases the selectivity of such biosensors complicating their practical applications [5]. Electrochemical properties of GNPs can be exploited to develop more selective biosensors for the determination of diagnostic targets [11,12]. The oxidation of GNPs and reduction of gold ions are commonly performed in electrochemical biosensors to produce appropriate analytical signal [9–12].

The above applications of GNPs generally assume their conjugation with biospecific proteins such as antibodies, streptavidin, and protein A to ensure the specificity of developed probes. The conjugation strongly influences the structural and physicochemical properties of GNPs and therefore the performance of GNP–protein complexes as biosensor probes. The dependence of light-absorptive and scattering parameters of GNPs on protein dielectric environments, studied in detail earlier [2,8,13,14], is commonly exploited in biosensor applications [8] as well as for the verification of GNP–protein complexes used in biomedical research [1]. There is a lack of similar studies concerning the effects of protein nanoenvironment on the electrochemical performance of GNPs.

Here, we present the comparative study of voltammetric properties of GNPs and their complexes with several proteins on glassy carbon and carbon nanotube-modified electrodes. The main objective

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doi:10.1016/j.bioelechem.2009.06.002